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OCTAHEDRAL MO6 CLUSTERS SUPPORTED BY METHOXIDE LIGANDS

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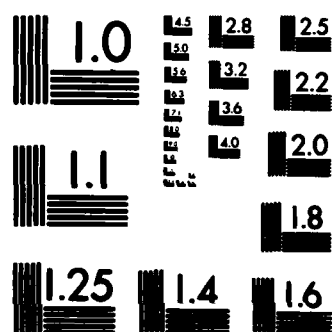
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OCTAHEDRAL Mo_6 CLUSTERS SUPPORTED BY METHOXIDE LIGANDS

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The structures of the $[\text{Mo}_6(\mu_3\text{-Cl})_8(\text{OMe})_6]^{2-}$ and $[\text{Mo}_6(\mu_3\text{-OMe})_8(\text{OMe})_6]^{2-}$ anions have been determined and reveal interesting comparisons of M-M and M-O distances with related $\text{Mo}_6(\mu_3\text{-X})_8^{4+}$ containing compounds and polynuclear alkoxides of molybdenum. ←		

A recent report¹ emphasized the importance of metal-metal bonding in the chemistry of molybdenum and tungsten alkoxides and noted that the only examples of alkoxides of molybdenum(II) were described² in 1968 as products obtained from the reactions between molybdenum(II) halides and NaOMe in methanol. Depending upon the reaction conditions, two types of compounds were isolated, namely, $\text{Na}_2\text{Mo}_6\text{X}_8(\text{OMe})_6$ and $\text{Na}_2\text{Mo}_6(\text{OMe})_{14}$. These were suggested to be structurally related to other well known $\text{Mo}_6(\mu_3\text{-X})_8^{4+}$ containing compounds which have a 24 electron octahedral Mo_6 cluster inscribed within a cube of triply bridging halide ligands.³ We report here a structural study which confirms this original suggestion and reveals some fascinating structural effects.

Following the literature procedure,² crystals of $2\text{Na}^+(\text{MeOH})_{10}[\text{Mo}_6\text{Cl}_8(\text{OMe})_6]^{2-}$ were obtained from methanol solution and one crystal was transferred to the goniostat of the diffractometer and cooled to -160°C in a liquid-nitrogen boil-off cold stream.⁴ The following cell parameters were determined: $a = 12.218(4) \text{ \AA}$, $b = 10.603(7) \text{ \AA}$, $c = 10.673(3) \text{ \AA}$, $\alpha = 59.46(2)^\circ$, $\beta = 76.80(2)^\circ$, $\gamma = 84.70(2)^\circ$, $Z = 1$, $d_{\text{calcd}} = 2.023 \text{ g cm}^{-3}$ and space group $\text{P}\bar{1}$. Using 2915 reflections having $F > 2.33\sigma(F)$ out of a total of 3051 unique intensities (collected by scan techniques, $\text{Mo K}\alpha$, $6^\circ < 2\theta < 45^\circ$), the structure was readily solved by Patterson techniques and Fourier syntheses. All atoms, including hydrogen atoms, were located and refined. Final residuals are $R(F) = 0.026$ and $R_w(F) = 0.036$. The structure consists of $[\text{Mo}_6(\mu_3\text{-Cl})_8(\text{OMe})_6]^{2-}$ anions within a lattice of extensively hydrogen bonded MeOH with each Na^+ ion being surrounded by five MeOH molecules. An ORTEP view of the centrosymmetric molecule is given in Figure 1.

Crystals of $2\text{Na}^+(\text{MeOH})_{10}[\text{Mo}_6(\text{OMe})_{14}]^{2-}$ were similarly obtained from methanol and examined at -160°C . Crystal data: $a = 12.199(2) \text{ \AA}$, $b = 11.500(3) \text{ \AA}$, $c = 18.689(5) \text{ \AA}$, $\beta = 88.47(1)^\circ$, $Z = 2$, $d_{\text{calcd}} = 1.744 \text{ g cm}^{-3}$ and space group $P2_1/n$. Using 2687 reflections having $F > 2.33\sigma(F)$ from a total of 3416 unique intensities (collected by scan techniques $\text{Mo K}\alpha$, $6^\circ < 2\theta < 45^\circ$), the structure was solved by a combination of direct methods and Fourier syntheses. Hydrogen atoms for all methyl groups were located in a difference Fourier phased on the refined non-hydrogen atom parameters. While several possible peaks in the final difference Fourier could be assigned to hydroxyl hydrogens, they were questionable at best and were thus ignored. Final residuals are $R(F) = 0.045$ and $R_w(F) = 0.045$. The structure consists of $[\text{Mo}_6(\mu_3\text{-OMe})_8(\text{OMe})_6]^{2-}$ anions within a lattice of extensively hydrogen bonded methanol and solvated Na^+ ions.

In the $[\text{Mo}_6(\mu_3\text{-Cl})_8(\text{OMe})_6]^{2-}$ structure, O(9) and O(10) are H bonded to one MeOH each, while O(8) is bonded with two MeOH molecules. In the $[\text{Mo}_8(\mu_3\text{-OMe})_8(\text{OMe})_6]^{2-}$ structure where the hydroxyl hydrogens were not located and refined, one may infer the existence of hydrogen bonds based on O---O separational distances.⁵ Specifically, an O---O separation of 3.0 \AA or less implies an O--H---O interaction. In this way we infer that O(4) and O(8) are both H bonded to two MeOH molecules while O(6) is H bonded with only one.

Pertinent averaged structural data for the Mo_6 -methoxide anions are presented in Table I along with those for related halo species. A number of fascinating features emerge. (1) The substitution of terminal OMe ligands for terminal chlorides causes little change in M-M distances, but replacement of the $\mu_3\text{-Cl}$ group by $\mu_3\text{-OMe}$ causes a substantial shortening. This is expected as MO distances are substantially shorter (by ca. 0.3 \AA) than MCl distances. (2) The terminal M-X

bond distances are only marginally longer than the bridging (μ_3) M-X distances. This is true for the $\text{Mo}_6\text{Cl}_{14}^{2-}$ and the $\text{Mo}_6(\text{OMe})_{14}^{2-}$ anions. Generally one observes that M-X bridging distances are significantly longer than terminal distances.⁶ For example in the compounds $\text{Mo}_3(\mu_3\text{-O})(\mu_3\text{-OR})-(\mu_2\text{-OR})_3(\text{OR})_6$ where R = i-Pr or (CH₂-t-Bu), one finds $\text{Mo-O} < \text{Mo-}\mu_2\text{-O} < \text{Mo-}\mu_3\text{-O}$ with roughly 0.1 Å difference between each type of alkoxide.⁷ (3) The substitution of $\mu_3\text{-Cl}$ by $\mu_3\text{-OMe}$ causes the Mo-O terminal distances to increase by close to 0.1 Å. (4) An inspection of the individual terminal Mo-O distances (see captions to figures) shows that oxygen atoms which are hydrogen bonded to two MeOH molecules have longer Mo-O bonds, by roughly 0.05 Å, than those which are only hydrogen bonded to one MeOH molecule.

It should also be noted that these are the longest Mo-O distances seen thus far in the chemistry of molybdenum alkoxides.⁶ In part, this may be attributable to the fact that the terminal ligands are H bonded with solvent MeOH molecules. However, we believe that there are electronic factors operating between the radial (terminal) RO ligands and the 24 electron Mo_6 cluster⁸ which also cause these Mo-O bonds to be unusually long. First, there is competition for use of molybdenum d_{z^2} and p_z atomic orbitals in a σ bonding sense, i.e. a mutual trans-influence, between strong cluster bonding and strong metal-ligand bonding. Second, the molybdenum d_{xz} and d_{yz} atomic orbitals are extensively used in M-M bonding and are thus not available for RO-to-Mo π -bonding.⁹ Indeed the latter becomes a repulsive effect. In going from $\mu\text{-Cl}$ to $\mu_3\text{-OMe}$, the M-M interactions become stronger as a result of the contraction of the Mo_6 cluster and thus the Mo-O terminal bond distances are lengthened.

Clearly a more quantitative examination of the bonding in these Mo_6 -alkoxide clusters is warranted. Also, their electrochemical and photo-excited state chemistry is of interest, if only to provide a comparison with the unusual properties already noted for the $\text{Mo}_6\text{X}_{14}^{2-}$ anions ($\text{X} = \text{Cl}, \text{Br}$).¹⁰ Finally, the high reactivity of the alkoxy ligands toward ligand substitution reactions leads us to suggest that these alkoxides should be good materials for syntheses and exploration of new Mo_6 -cluster chemistry. These studies are underway.

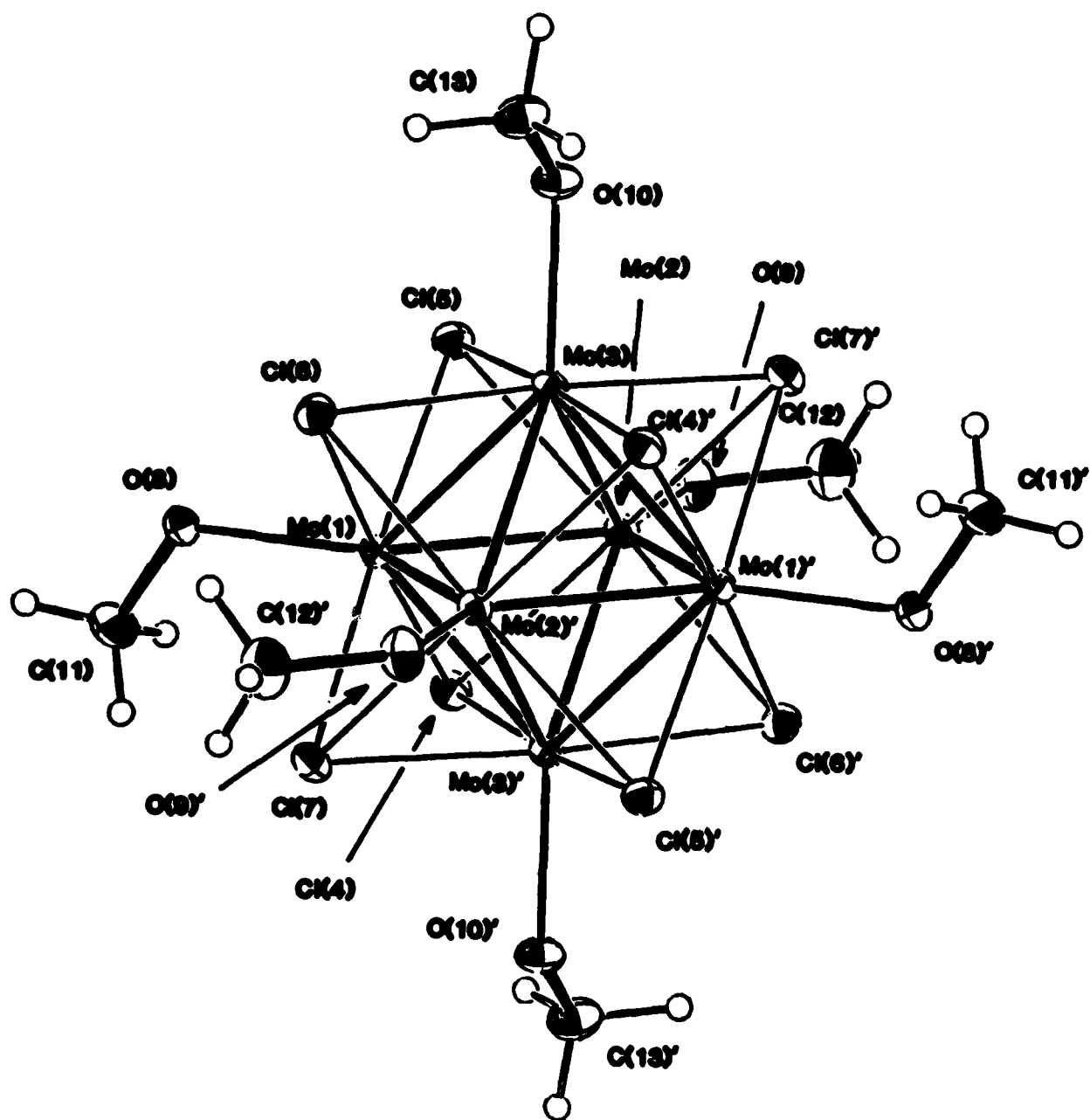
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Supplementary Materials Available. Tables of fractional coordinates and thermal parameters have been deposited with the Cambridge Crystallographic Data Center. Complete structural information is available, in microfiche form, from the Indiana University Chemistry Library, Bloomington, Indiana 47405, at a cost of \$ 2.50 per structural report. For $2\text{Na}^+[\text{Mo}_6(\mu_3\text{-Cl})_8(\text{OMe})_6]^{2-} \cdot 10\text{MeOH}$, request MSC No. 83047, and for $2\text{Na}^+[\text{Mo}_6(\mu_3\text{-OMe})_8(\text{OMe})_6]^{2-} \cdot 10\text{MeOH}$, request MSC No. 83053.

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9. The six molybdenum (d_{xz} , d_{yz}) atomic orbitals make significant contributions to the filled molecular orbitals t_{1u} , t_{2g} and t_{2u} , all having cluster bonding character, and one unfilled low lying t_{1u} anti-bonding orbital. While the interaction of the six radial (terminal) ligands with the $\text{Mo}_6(\mu_3\text{-X})_8^{n+}$ moiety greatly destabilizes the a_{1g} bonding orbital and the e_g and t_{1u} antibonding orbitals, which have significant d_z^2 contributions, it has little apparent effect on bonding orbitals having (d_{xz} , d_{yz}) character. However, the latter have appropriate symmetry to interact with $p\pi$ orbitals on the radial ligands. If the ligand $p\pi$ orbitals are filled, there would be a destabilization of the M-M bonding t_{1u} and t_{2u} orbitals.
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Figure 1. An ORTEP view of the $[\text{Mo}_6(\mu_3\text{-Cl})_8(\text{OMe})_6]^{2-}$ anion found in the salt $2\text{Na}^+ \cdot 10\text{MeOH} \cdot \text{Mo}_6\text{Cl}_8(\text{OMe})_6^{2-}$ showing the atom number scheme. Pertinent bond distances (Å) are $\text{Mo}(1)\text{-O}(8) = 2.080(3)$, $\text{Mo}(2)\text{-O}(9) = 2.032(3)$, $\text{Mo}(3)\text{-O}(10) = 2.038(3)$.

Figure 2. An ORTEP view of the $[\text{Mo}_6(\mu_3\text{-OMe})_8(\text{OMe})_6]^{2-}$ anion in the salt $2\text{Na}^+ \cdot 10\text{MeOH} \cdot \text{Mo}_6(\text{OMe})_{14}^{2-}$ showing the atom number scheme. Pertinent bond distances (Å) are $\text{Mo}(1)\text{-O}(4) = 2.150(6)$, $\text{Mo}(2)\text{-O}(6) = 2.092(6)$, $\text{Mo}(3)\text{-O}(8) = 2.149(6)$.



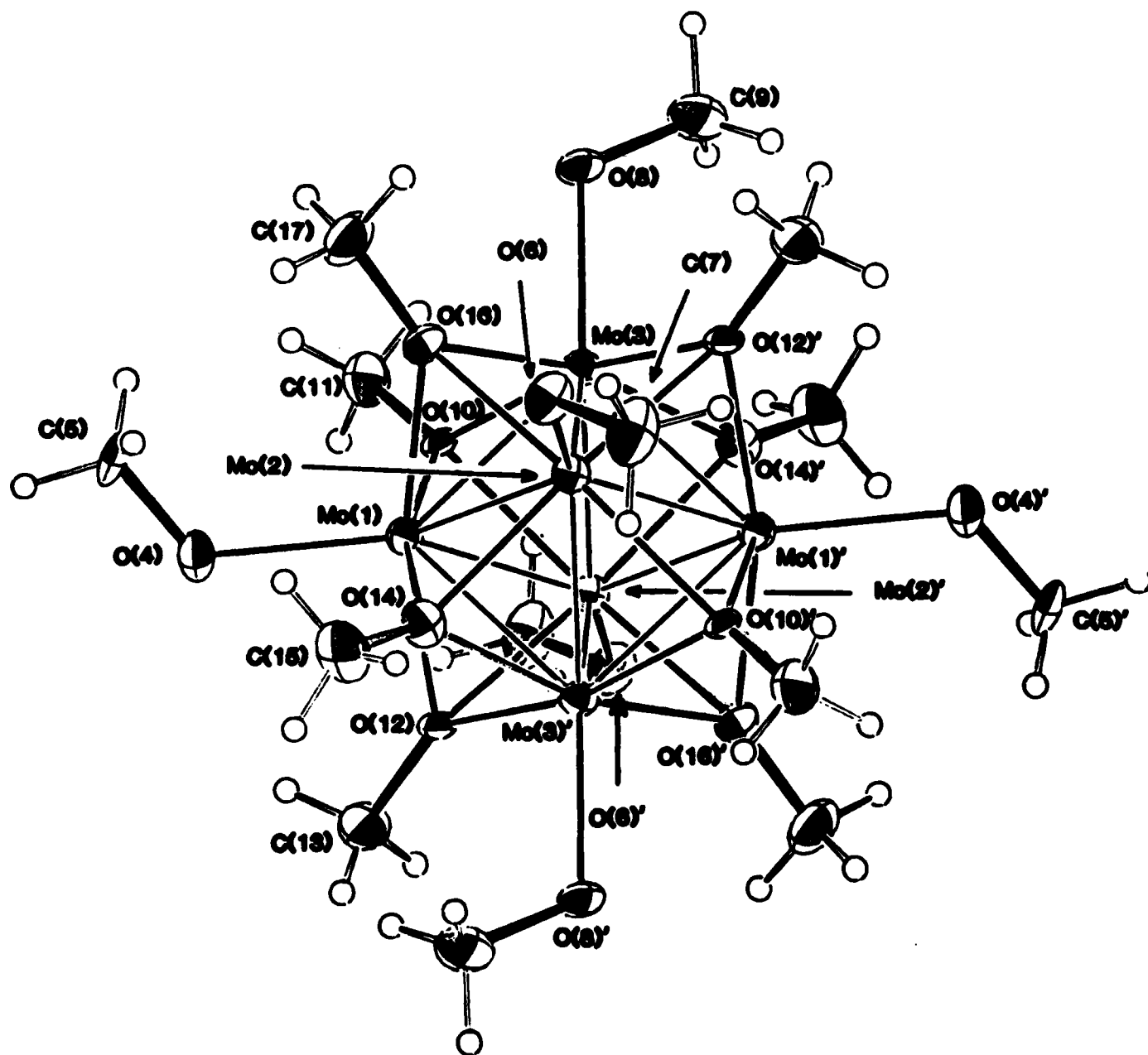


Table 1. Comparison of Some Pertinent Structural Parameters in Octahedral Mo₆ Halide and Alkoxide Clusters.

Compound	Mo-Mo Distance (Ang.)	Mo-X Distance (Ang.)	Mo-X Distance (Ang.)	Mo-O - R Angle	Mo-X Mo Angle	Reference
HgMo ₆ (μ ₃ -Cl) ₈ Cl ₆	2.62 ± 0.01	2.50 ± 0.02	2.48 ± 0.02	—	—	1
Na ₂ Mo ₆ (μ ₃ -Cl) ₈ (OMe) ₆	2.607 ± 0.004	2.051 ± 0.029	2.490 ± 0.006	126.0	63.0	This work
Na ₂ Mo ₆ (μ ₃ -OMe) ₈ (OMe) ₆	2.536 ± 0.008	2.130 ± 0.038	2.173 ± 0.013	119.9	71.3	This work
Mo ₆ (μ ₃ -Br) ₈ Br ₄ (H ₂ O) ₂	2.640 ± 0.002 (2.630 ± 0.002)	2.587 ± 0.002 (Mo-Br)	2.606 ± 0.002	—	—	2

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